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Microemulsions – A Brief Introduction

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1. Introduction

Nevertheless, the existence and application history of the microemulsions goes back to the very older times, but the oldest available reports in this field have been published by Schulman (Schulman & Hoar, 1943) and Winsor (Winsor, 1954). Their works are the starting point of efforts for the systematic understanding of the microemulsions. Meanwhile, the widespread generalization and applications of these systems have been started in the late 1970s, with their use for the enhanced oil recovery during the energy crisis.

The term of microemulsion applies to a mixture with at least three components; an oily phase, an aqueous phase and a surface active species, so called surfactants. Sometimes the forth component i.e., co-surfactant can/must be present (Saito & Shinoda, 1967. Saito & Shinoda, 1970). Depending on the ratios between the components, in the two extremes the microstructure of the microemulsions vary from a very tiny water droplets dispersed in oil phase (w/o microemulsion) to a oil droplets dispersed in water phase (o/w microemulsion). The microstructure of the mixture changes continuously from one to another extreme, namely, from a spherical to cylindrical, tubular and interconnected continuous oil and water phases separated with a very thin layer of surfactant molecules, in the middle, which is defined as bicontinues microemulsion (Scriven, 1976). The microemulsions of each kind are thermodynamically stable and transparent solutions. There are main differences between emulsions and microemulsions in terms of structure and stability. In contrast to the microemulsions, the emulsions are unstable systems and without agitation, phase separation will occur in them. The other difference is that the size of droplets in emulsions are in the range of micrometers, while in microemulsions the size of micelles are in the range of 5-100 nm, depending on the some parameters such as surfactant type and concentration, the extent of dispersed phase (Prince 1977, Hou et al., 1988, Maitra, 1984). Hence, sometimes the microemulsion term is misleading, because it doesn't reflect the size of dispersed phase droplets in the system which, are in the nanometer range. Depending on the type of the surfactants employed in the preparation of the microemulsion, another important parameter that affects the main characteristics of a microemulsion is the presence of electrolytes in the aqueous phase.

2. Phase diagrams and types of microemulsions

The formation of the thermodynamically stable microemulsions require that an adequate amount of the corresponding components must be mixed. Determination of these proper compositions is an important issue in this field to obtain the microemulsions with required properties. For this purpose, one must prepare mixtures with different compositions of the components, and check them regarding the type and number of phases present in the system. The resulting diagrams, showing the number/or type of phases present in the system associated with each specific composition, are called phase diagrams. From the industrial and application point of view, this process is called formulation, which indicates the specific compositions of the components giving a stable mixture effective in the concerned property. A number of different methodologies have been used for determination of the phase diagrams. Almost the earliest studies about the phase diagrams of the microemulsions can be found in the 1960s (Ekwall et al., 1960). Using the phase diagrams, it has been confirmed that the Schulman's so-called micromulsion is not an emulsion but a solubilized solution (Shinoda & Kunieda, 1973). The mechanism of the microemulsion formation has been studied in connection with the phase diagrams and the relation between the amounts of components required to form a clear microemultion has been understood from the phase diagrams (Ahmad et al., 1974). They have studied the phase diagrams of different systems with anionic, cationic and non-ionic surfactants, and could obtain maximum solubillization with the optimum ratio of the surfactant and co-surfactant. By a detailed investigation on pseudoternary phase diagrams of two microemulsion systems it has been evidenced that a great variety of phases is present. They have concluded that the interaction between water and oil domains is an important parameter affecting the stability of microemulsions (Roux et al., 1983). The phase diagrams of the ternary system containing water-sodium alkylbenzene sulfonate (NaDBS)-hexanol and their quaternary system with xylene have been prepared at three different temperatures. The formation of different phases, such as microemulsion phase, reverse micelle phase was observed which have been qualitatively examined by optical (phase contrast and polarizing) microscopy or low angle X-ray diffraction. According to the results the amount of microemulsion phase was decreased by increasing of the temperature at surfactant concentrations of lower than 15% (Baker et al., 1984). The phase diagrams of the systems with alkyl polyether surfactants have been studied extensively in different aspects, (Zhao et al., 2011, Lang, 1999. Balogh, 2010, Selivanova et al., 2010, Magno et al., 2009, Boonme et al., 2006, Mitra & Paul, 2005, Lim et al., 2005).

The effect of addition of inorganic salts into the aqueous phase of the microemusions have been studied using phase diagrams. It has been observed that the added salts has a great influence on the solubilisation ability of the microemulsion system (Komesvarakul et al., 2006, Wei et al., 2005, Li et al., 2003, Van Nieuwkoop & Snoei, 1985, Yu et al., 2009, Chai et al., 2009, Qin et al 2008, Nedjhioui et al., 2007, Koyanagi et al., 2007, Mitra & Paul, 2005, Shinoda, 1967, Shinoda & Saito, 1968). As an example, it has been observed that the addition of salt shifts the fish diagram towards more hydrophobic oil systems and higher surfactant concentrations will be required (Komesvarakul et al., 2006). Determination of the phase diagrams has been used also as the bases for the applications of the microemulsion for the preparation of the nanoparticles (Najjar & Stubenrauch, 2009, Magno et al., 2009a). Here, the phase diagrams have been used to select the proper compositions of the microemulsions to get spherical well defined micelles, and consequently resulting nanoparticles.

3. Thermodynamics of microemulsions

The microemulsions are thermodynamically stable mixtures of oil, water and one /or more surface active agents (surfactants). For understanding of the thermodynamics of the microemulsions one must consider all kind of the interactions existing between the components present in the system, i.e. oil, water, surfactant (and co-surfactant) and the microstructures (micelles, globules, lamellar and …) formed in the system with each other and the media. The theoretical aspects of the stability of microemulsions is a well known issue (Kumar & Mittal, 1999).

Nevertheless, the nature of the interactions between oil and water are repulsive forces, the presence of the surfactant molecules changes the balance between the forces towards the attractive forces. The stabilizing effect of the surfactants is exerted by the formation of the different types of microstructures to favour the stabilizing interactions. Hence, the understanding of the microstructure of the microemulsion systems is of prime importance.

Almost the first speculations about the microstructures of the microemulsion consisting of the surfactant, oil and water have been made in 1950s (McBain, 1950, Philipoff, 1951, Becher, 1968, Shinoda, 1970). In the meantime, the first accurate thermodynamic data about a microemulsion system have been reported in 1960s. Based on those data Shinoda has developed an acceptable model, which could reasonably explain this dissolution phenomenon by formation of the structures such as log-boom (Becher, 1968), lamellar (McBain, 1950), cylindrical, spherical, ellipsoidal, or rodlike micelles (Shinoda, 1970). Many reports can be found in the literature about the thermodynamic stability considerations of the different microemulsion systems (Ruckenstein, 1981, Bennett et al., 1981, Bellocq et al., 1982, Prouvost et al., 1985, Biais et al., 1987, Mukherjee et al., 1997, García-Sánchez et al., 2001, Fu et al., 2002, 2003).

For modeling of phase behavior, Bennett et al was presented a mathematical framework in a way consistent with the thermodynamically required critical tie lines and regarding critical endpoints. The modeling of surfactant-rich third phase evolution were extended to satisfy these requirements and also Hand's scheme for modeling of binodals and Pope and Nelson's approach was regarded (Bennett et al., 1981). It has been presented that the model-generated progressions of ternary phase diagrams gives a better understanding of the experimental data and reveals correlations of relative phase volumes (volume uptakes) with other phsae diagrams parameters.

In recent years, kartsev et al have used a two-phase model to approach to the thermodynamics of microemulsions (Kartsev et al., 2010). They proposed dispersion medium as one phase and the sum of disperse phase nanodrops as the second phase.

The performance of model was evaluated with experimental data and it was proved that the use of this model to solve microemulsion thermodynamics problems quantitatively gives satisfactory results with model inadequacy not more than 10%.

4. Techniques for investigation of microemulsions microstructure

In the course of development of the microemulsions, different techniques has played an important role in this process and helped scientists to understand the different aspects of microemulsion science.

Nuclear magnetic resonance (NMR) and infrared spectroscopy are among the oldest techniques used for the investigation of microemulsions. Using NMR measurements, Gilberg and co-workers have indicated that in case of micelles with a larger water core the packing density of surfactant molecules is low, and consequently the stability of such micelles are lower than the micelles with higher packing density (Gillberg et al., 1970). Stilbs has demonstrated that by solubilization of the short-chain *n*-alcohols in microemulsions containing SDS micelles the 1H NMR line broadening occurs (Stilbs, 1982). He concluded that the results are indication of the highly disordered structures only, and the addition of the short-chain n-alcohols causes the breakdown of the micelles. Also, it was shown that by increasing of the surfactant concentration the growth in micellar size occurs progressively, and at higher concentrations long prolate-shaped aggregates form. The addition of water to the bicontinuous microemulsions, studied by 13C-NMR chemical shift trends of C8G2 and pentanol carbons, indicated a reduction in the mean surfactant film curvature towards water (Parker et at., 1993). The measurement of the rotational correlation time (τ) of a nitroxide labeled fatty acid probe, 5-doxyl stearic acid, versus cetyltrimethylammonium bromide (CTAB) (as surfactant) concentration in aqueous solution has been done via ESR spectroscopy (Li et al., 1997).

The CMC value obtained by this method has been in good agreement with the surface tenstion measurements. Using 2H NMR studies, it was indicated that five water molecule are tightly bound to each CTAB molecule. The chemical shifts and T1 relaxation time data obtained by 1H NMR measurements were used to investigate the microemulsion properties and structure (Waysbort et al., 1997, Bastogne et al., 1999, Kataoka et al., 2007, Causse et al., 2006).

Investigaton of the microemulsions containing didodecyldimethylammonium sulfate (as surfactant), water and dodecane /or hexadecane by NMR self-diffusion approach, has revealed that diffusion coefficients for the surfactant and oil are equal at high surfactant-to-oil ratios. This observation indicates that the structure is truly bicontinuous over distances on the order of µm in such a system (Söderman & Nydén, 1999). The existence of a worm-like structure in the intermediate water contents instead of the classical bicontinuous structure was proposed, which is confirmed by SAXS and SD-NMR analysis (Libster et al., 2006). There are many other reports in the literature about the studying of the microstructure and other properties of the microemulsion systems. Among them are the studyng of the competitive solubilization of cholesterol and phytosterols in nonionic microemulsions by pulse gradient spin-echo NMR (Rozner et al., 2008), study of the microstructure of four-component sucrose ester microemulsions using SAXS and NMR measurements (Fanun 2001), solution properties of C18:1E10/oil/water system by PGSE-NMR self-diffusion (Ko et al., 2003), reverse micelles of di-isobutylphenoxyethoxyethyl-dimethylbenzylammonium methacrylate in benzene (Emin et al., 2007).

Another type of techniques that have played an important role in understanding of the microemulsions, is the methods developed for visualization of microemusion micro-structures. These techniques based on the transmission electron microscopy (TEM) images prepared from a very thin film of the samples. This type of techniques is consisted of three different methods: a) freeze fracture electron microscopy (FFEM) (Jahn & Strey, 1988, Burauer et al., 2003), b) Cryo-Direct Imaging (Cryo-DI) (Talmon, 1999, Bernhein-Grosswasser et al., 1999) and c) freeze-fracture direct imaging (FFDI) (Belkoura et al., 2004). The first of these techniques was introduced by Jahn and Strey in 1988 (FFEM) (Jahn & Strey, 1988, Jian et al., 2001). Development of these techniques along with the other techniques helped the scientists in well understanding of microstructure of microemulsions. Later on, these techniques has been developed/used by other researchers to investigate the microemulsions (Agarwal et al., 2004, Ponsinet & Talmon, 1997, Hellweg et al., 2002, Yan et al., 2005, Mondain-Monval, 2005, Zhang et al., 2010, Klang et al., *2012*)

The use of cryo-field emission scanning electron microscopy (cryo-FESEM), in combination with the other techniques, has been reported by Boonme et al. for investigation and characterization of microemulsion structures in the pseudoternary phase diagram of isopropyl palmitate/water/Brij 97:1-butanol system (Bonne et al., 2006, Krauel et al., 2007). According to the photomicrographs made using cryo-FESEM technique, in microemulsions with higher than 15% wt/wt water contents the formation of globular structures have been observed (Sai et al., 2006, Lu et al., 2006, Anouti et al., 2012, Krauel et al., 2005, Kapoor et al., 2009, Lutter et al., 2007, Holland & Warrack, 1990).

The other type of methods which have played a significant role in the characterization of the microemulsions is the scattering techniques, such as dynamic light scattering and neutron spin-echo spectroscopy (Hellweg & Langevin, 1998, Nagao et al., 1997, Nagao et al., 2006, Geyer et al., 2004, Gradzielski & Langevin, 1996, Hellweg et al., 2001, Hellweg et al., 2001, Magid, 1986, Tabony et al., 1983, Atkinson et al., 1988, Magid et al., 1983, Chen, 1986, De Geyer & Tabony, 1986), light scattering (Attwood & Ktistis, 1989, Guest & Langevin 1986, Aoudia et al., 1991, Zhang & Michniak-Kohn, 2011, Li et al., 2010, Xie et al., 2007, Ben Azouz et al., 1992, Zemb, 2009, Magid, 1986, Kljajić et al., 2011, Tan et al., 2011, Wadle et al., 1993, Dave et al., 2007, Kataoka et al., 2007, Silas & Kaler, 2003, Wines & Somasundaran, 2002, Fanun, 2008, Hellweg et al., 2001, Fanun et al., 2001).

5. Surfactants

The surfactants are molecules with at least two parts, one part soluble in polar solvents (hydrophilic) and the other part insoluble in the polar solvent (hydrophobic). Because of this double character, the term amphiphile is also used as synonym with surfactant (Holmberg et al., 2002). The polar part of the surfactant molecule is referred as head, and the non-polar part of the molecule as tail. Having these two parts with opposing solubilisation abilities, gives the surfactant molecules unique capabilities, such as tendency to adsorb at the surfaces and interfaces, which results in the decrease of the surface tension, and also formation of the aggregates inside the solutions, resulting in the formation of the microemulsions. This double character of the surfactant molecule enables it to orient in desired way while in contact with the two phases with different hydro/lypophilic properties, or to make aggregates inside of the solution with hydro- or lypophilic parts directed towards the media. Such aggregates can solubilise an oil in aqueous phase (micelles) or water in the oily phase (reversed micelles).

The polar nature of the head group of surfactants vary from non-ionic to ionic character. Depending on the nature of this part, the surfactants are categorized into non-ionic, anionic, cationic and amphoteric (zwitterionic) surfactants (Tadros, 2005, Rosen et al., 2000, Os, 1998). Versatile types of functional groups have been utilized as the head group for the surfactants. Among them carboxylates, sulphates, phosphates, sulfonates, quaternary amines, polyethers have a great importance in many different applications. Commercially used surfactants can be obtained from synthetic or natural resources

(Hayes et al., 2009, Nace et al., 1996, Goodwin 2004, Holmberg 1998). Regarding the structure, surfactants can be simple molecules, like sodium or potassium salt of the carboxylic acids generally with 12-18 carbon atoms, or polymers with various molecular weights (Kwak 1998, Hill 1999, Malmsten, 2002,). For any application of the surfactants one should evaluate the issues concerned with that special case, as the toxicity, stability and performance of the surfactants is closely related to its structure (Esumi & Ueno, 2003, Dias & Lindman 2008).

6. Microemulsions in non-conventional systems

Ionic liquids and supercritical fluids are widely used non-conventional systems which have been used in many different fields of applications, as well as microemulsion research (Zhang et al., 2006, Tingey et al., 1991, Eastoe et al., 1991, Johnston et al., 1996). Among the supercritical fluids, carbon dioxide, because of its non-toxicity, cheapness and easy availability, has been used as solvent for different purposes, such as extraction and polymerizations. One of the main issues in using the supercritical carbon dioxides as solvent is that for the high molecular weight polymeric compounds it has lower solubilising power. Hence, for this type of applications design and synthesis of special surfactants is of prime importance (Najjar 2006, Beginn et al., 2006). The effect of supercritical conditions on the microemulsions and formation of the micelles in this type of solvents such as sc-ethane, sc-propane has been studied (Kumar & Mittal, 1999, McFann & Johnston, 1993, Beckman et al., 1991, Bartscherer et al., 1995, Schwan et al., 2010). Use of general low molecular weight surfactants such as sodium bis-2-ethylhexyl sulfosuccinate (AOT) (Kotlarchyk et al., 1985, Olesik & Miller, 1990, Zulauf & Eicke, 1979, Yazdi et al., 1990), poly(ethylene oxide) alkyl ethers (C_nE_m) (Johnston et al., 1989, Yee et al., 1992, Eastoe et al., 1990, Klein & Prausnitz, 1990), fluorinated analogues of AOT (Park et al., 2006) and flouropolymers based surfactants are the most widely used surfactants in supercritical hydrocarbon fluids (ethane and propane) (Eastoe et al., 2001, Eastoe et al., 2006, Hoefting et al., 1993).

Supercritical carbon dioxide is also one the widely used sc-fluids in microemulsion science. Because of the lack of favourable interactions between CO_2 and most of compounds, the commercially available general surfactants have not performed well in sc-CO_2. Meanwhile formation of the some microstructures similar to micelles has been evidenced in sc-CO_2 (Randolph et al., 1987, Ritter & Paulaitis, 1990, Iezzi et al., 1989, Oates 1989, Consani & Smith, 1990, Eastoe et al., 2001, Sagisaka et al., 2003, Klostermann et al., 2011). Many research activities have been done examining the performance of a lot of commercially available surfactants in sc-CO_2, mostly showing very low effect on the increasing of solubilisation of polar compounds (such as water) in the solvent. As mentioned previously, by the design of special surfactants, mainly based on the flouropolymers one can improve the micelle formation, and consequently solubilisation of the more polar compounds in sc-CO_2 phase (Eastoe 2006). Various techniques have been used for the investigation of the microstructure of microemulsions in supercritical fluids. Among them are the time-resolved fluorescence spectroscopy using coumarin 480 (Pramanik et al., 2010), pyridine N-oxide (Simón de Dios & Díaz-García, 2010, Yazdi et al., 1990, Zhang & Bright, 1992a, 1992b, López-Quintela et al., 2004), pyrene (Nazar et al., 2009) or Ti(IV) complexes (Chem et al., 2009) as fluorescence probe, FT-IR spectroscopy (Yee et al., 1991, 1992, Takebayashi et al., 2011), small-angle neutron scattering (SANS) measurements (Eastoe et al., 1996, Zielinski et al., 1997, Cummings et al., 2012, Torino et al., 2010, Frielinghaus et al., 2006), electron paramagnetic resonance (EPR) spectroscopy (Johnston et al., 1996), small-angle X-ray scattering (SAXS) (Fulton et al., 1995, Kometani et al., 2008, Akutsu et al., 2007), near-infrared spectroscopy (Takebayashi et al., 2011), and high-pressure NMR (Thurecht et al., 2006), which have been extensively employed for investigation of these systems.

The earliest theoretical studies of microemulsions in supercritical fluids was reported in 1990s showing a good agreement between theory and experimental results, among them are the works of Johnston et al. (Peck & Johnston, 1991). Different models have been examined and the results compared to be in different levels of agreement with the experimental data (García-Sánchez et al., 2001, Taha et al., 2005, Ganguly & Choudhury, 2012).

A lots of reports can be found in the literature about the application of microemulsions prepared in supercritical fluids for different purposes, such as, investigation of sustained release of nucleic acids from polymeric nanoparticles prepared in sc-CO_2 microemulsions (Ge et al., 2010), biocatalysis using lipase encapsulated in microemulsion-based organogels in sc-CO_2 (Blattner et al., 2006), continuous tuning of size CdS and ZnS nanoparticles in a water-in-sc-CO_2 microemulsion (Fernandez & Wai, 2007), and synthesis of nanoporous clusters of zirconia (ZrO_2) (Lee et al., 2010).

7. Some applications of microemulsions

7.1 Industrial applications

Microemulsions play a great role in the everyday life of human body. There are many final products which, in principle based on the microemulsions and/or they are somehow in very close relation with the microemulsions. Sometimes the microemulsion formation is the important process that, occur at the final stage of the application. However, in every case the formation of the microemulsion results in the solubilisation of the chemicals which may be the active agent or the unwanted compound that its removal is the first task of the process. Or in some cases this solubilisation helps to deliver the active agents to the required sites. Any formulation which intended to be used in industrial scale should be economical. Various types of cleaning process are one of the main areas that relates to the application of the microemulsions in big scales. Some of the other areas include: agrochemicals formulations (Mulqueen 2003, Chen et al., 2000) (solubilizing organic agrochemicals in water), preparation of the vaccine adjuvants to improve the effectiveness of the active compounds (O'Hagan et al., 1997, Hariharan & Hanna, 1998), micro and -emulsion polymerization (Xu & Gan, 2005, Capek 2001), floatation process in the pulp and paper industry, concrete and asphalt, petroleum industry (for example in enhanced oil recovery, natural gas dehydration and etc.) (Santanna et al., 2009, Austad & Taugbøl 1995), firefighting foams, defogging agents, decontamination of the media from chemical and biological agents and many more other application (Solans & Kunieda, 1997). Also, formulation of the cosmetics (Valenta & Schultz, 2004), medicals and food additives are the other important areas that require very exact control and analysis. According to the statitistics, in 2003 about 2 milion m^3 of surfactants, made from fatty alcohols has been consumed (Brackmann & Hager, 2004). There are many more reports in the literature that indicate the importance and level of the applications of this type of compounds.

7.2 Applications in biological and health sciences

Because of many unique properties, such as stability, ability for solubilisation of the lypo- or hydrophilic compounds and etc, microemulsions has attracted a great attention for a several type of applications. Therefore, these mixtures have entered in many fields of research and applications, ranging from advanced oil recovery to delivering genes into the cells. The ability to formulate such mixtures with biocompatible ingredients has made possible to use them in biological and health related areas extensively. Hence, microemulsions have found wide application in delivering drugs with different physical and chemical characteristics and different ways of delivering such as, oral delivery of protein drugs (Sarciaux et al., 1995, Ke et al., 2005, Cheng et al., 2008, Kim et al., 2005,), ophthalmic (Lv et al., 2005., Gulsen & Chauhan, 2005), transdermal (Kantaria et al., 1999, Kreilgaard et al., 2000, Sintov & Botner 2006, Neubert, 2011, Zhu et al., 2008), amphiphilic drugs (Djordjevic et al., 2004, Oh et al., 2011), internasal (Cho et al., 2012) or other ways (Zhou et al., 2011, Lawrence & Rees, 2000).

Besides drug delivery, microemulsions have many other applications in these fields. Among them is the delivering of genes into the cells (Gupta et al., 2004), with the aim of treatment of disease or diagnosis (Pedersen et al., 2006, Peng et al., 2006, Xu et al., 2011, Rossi et al., 2006, Santra et al., 2005), targeting cancer cell (Tao et al., 2011, Lu et al., 2008, Reithofer et al., 2011), act as vaccine (Sun et al., 2009, Mumper & Cui, 2003), biocatalyss (Stamatis & Xenakis, 1999, Zoumpanioti et al., 2010, Blattner et al., 2006), cosmetics (Chiu & Yang, 1992, Förster et al., 1995, Valenta & Schultz, 2004, Teichmann et al., 2007) or changing the genetic to improve the performance of the targeted cells (Kitamoto et al., 2009, Courrier et al., 2004).

Use of food grade components, oil and surfactant allows to prepare microemulsions which, can be added to foods and beverages (Rao & McClements, 2011, Zhang et al., 2008, Zhang et al., 2009, De Campo et al., 2004, Feng et al., 2009, Rao et al., 2012, Ziani et al., 2012, Flanagan et al., 2006).

7.3 Preparation and processing of nanomaterials

One of the other important fileds of applications of microemulsions is their use as media for the synthesis of different materials. Regarding the microstructure of the microemulsions one can choose a special formulation to have a well defined microstructure in the system. The microstructures which, are widely used in this respect are the water droplets in oil phase or oil droplets in water phase. As the size of this droplets are in the range of nanometer (about 5 to 50 nm), they act as nanoreactors dispersed in the oil or water media. This concept has been used extensively for the preparation of the many different type of materials, such as organic, inorganic, oxides, polymers and etc. in nanometer dimentions. Since last two decades and even now, this field is one of the hot research topics, specially for preparation of the nanomaterials. By this methodology, many researchers have prepared metallic and intermetallic nanoparticles (Aubery et al., 2011, Hosseini et al., 2011a, 2011b, Shokri et al., 2011, García-Diéguez et al., 2010), metal oxides (Tian et al., 2012, Du et al., 2012, Lin et al., 2012), metal salts (Dromta et al., 2012, Guleria et al., 2012, Esmaeili et al., 2011), polymers (Ouadahi et al., 2012, Ma et al., 2012, Mishra & Chatterjee, 2011, Elbert, 2011), luminescent nanoparticles (Probst et al., 2012, Darbandi et al., 2012), magnetic nanoparticles (Jing et al., 2011, Xu et al., 2011) and lipid nanoparticles for drug delivery (Puri et al., 2010, Seyfoddin et al., 2010, Das & Chaudhury, 2011). One of the other applications of microemulsions is to polymerize bicontinous microemulsions to obtain porous materials. This has been done by use of polymerizable surfactants, which their polymerization reaction can be started photochemically (Schwering, 2008, Ye, 2007, Stubenrauch et al., 2008, Chow & Gan, 2005, Magno et al., 2009b).

8. Theoretical studies on microemulsions

The microemulsions have been also studied theoretically and some models have been introduced for the theortical discussion on the microemulsions. The models such as continuum and lattice models, and models based on phenomenological free energy densities as well as those based on microscopic Hamiltonians have been proposed. These models mainly discuss about the parameters such as interfacial tensions, progression of microemulsion phase equilibria, and the wetting or non-wetting of the interfaces (Widom 1996). Boyden et al. has used the Monte Carlo method to simulate the oil/water miscibility gap, the coexistence of various phases, kinetics of micelle formation (Boyden et al., 1994). Most of the observed properties have been described very well by the proposed model. The phase behaviour of the microemulsions has been simulated by a mathamatical framework (Bennett et al., 1981), excess Gibbs energy models (García-Sánchez et al., 2001) and lattice Monte Carlo simulation (Behjatmanesh-Ardakani et al., 2008). In another study, Acosta has used the net-average curvature (NAC) model, introduced by his own research group (Acosta et al., 2003) to prepare the equation of state to fit and predict the phase behavior of microemulsions formulated with ionic surfactants (Acosta et al., 2008). In a work reported by Kiran et al. the morphology and viscosity of microemulsions has been studied using the HLD-NAC model (Kiran et al., 2010). They have introduced a new shapebased NAC model, relating the net and average curvatures to the length and radius of microemulsion droplets, with a hypothesized cylindrical core with hemispherical end caps.

Many of the reactions and processes in the microemulsions have been simulated using different models. The investigation of the drug release from drug loaded microemulsions (Grassi et al., 2000, Sirotti et al., 2002), nanoparticle precipitation using a population balance model (Niemann & Sundmacher, 2010), the formation of nanoparticles in mixing of two microemulsion systems by a Monte Carlo model (Jain & Mehra, 2004), time-evolution of the polymer particle size distribution (Suzuki & Nomura, 2003) and solubilization of oil mixtures in anionic microemulsions (Szekeres et al., 2006) have been perfomed theoretically.

9. Conclusions

In the same way as other fields, the science and technology of the microemulsions is a rapidly growing area, which gained a very high importance during last two decades. According to the scopus database, the number of papers published in the area of microemulsions, 1960-70s (112 papers), 1980s (974 papers), 1990s (2762 papers), 2000s (6933 papers) and 2011 (843 papers) shows a very high increasing rate. Besides the other parameters, the finding of many novel applications is one of the reasons for this fast delevolment in the area. The use of microemulsions in drug delivery systems and also in nanoscience and nanotechnology are among the most important applications, which attracted a high attention of the researchers. The possibility and easiness of the tuning of microemulsion properties with different parameters has allowed the scientists to use them in many interdisciplinary fields of research and applications. The future need for the developing of systems and materials with sustainablilty and biodegradability requires that biodegradable surfactants and compounds must be developed. Doing this, will be another reason increasing the importance of the microemulsions which can be used in bio systems.

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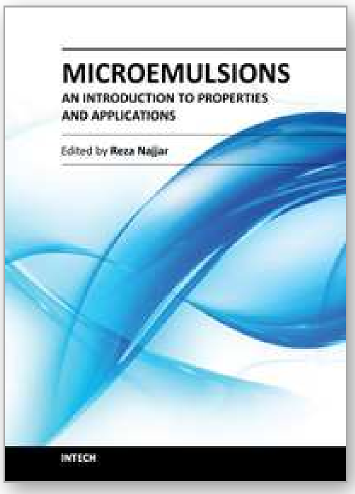

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The rapidly increasing number of applications for microemulsions has kept this relatively old topic still at the top point of research themes. This book provides an assessment of some issues influencing the characteristics and performance of the microemulsions, as well as their main types of applications. In chapter 1 a short introduction about the background, various aspects and applications of microemulsions is given. In Part 2 some experimental and modeling investigations on microstructure and phase behavior of these systems have been discussed. The last two parts of book is devoted to discussion on different types of microemulsion's applications, namely, use in drug delivery, vaccines, oil industry, preparation of nanostructured polymeric, metallic and metal oxides materials for different applications.

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